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SOUTHWEST MONSOON TRIGGERS RE-VOLATILISATION OF PERSISTENT ORGANIC POLLUTANTS FROM SOILS IN INDIA

G. Lammel[1], C. Degrendele[1], S.S. Gunthe[2], Q. Mu[1], A. Muthalagu[2], O. Audy[3], P. Kukucka[3], M.D. Mulder[3], M. Octaviani[1], P. Shahpoury[1]

[1]*Max Planck Institute for Chemistry, Multiphase Chemistry Department, Mainz, Germany*

[2]*Indian Institute of Technology, Environmental and Water Resources Engineering, Chennai, India*

[3]*Masaryk University, Research Centre for Toxic Compounds in the Environment, Brno, Czech Republic*

Introduction

Persistent organic pollutants such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) undergo long-range atmospheric transport, enhanced by multi-hopping (so-called 'grasshopper effect') and apart from source regions may also accumulate in remote areas, polar as well as mountain.[1-3] Off application areas, soil reservoirs fill through atmospheric deposition, followed eventually by re-volatilisation (soil-air gas exchange).[4-5] OCPs and PCBs had been heavily used in South Asia. DDT is still in use in India as insecticide in public health programmes. The direction of air-soil exchange of organic vapours can be sensitive to concentration in air[4].

We studied the influence of the onset of the southwest monsoon in southern India (arrival of clean southern hemisphere air) on POP cycling by field measurements and modelling.

Materials and methods

Air was sampled close to the town Munnar (10.093°N/77.068°E, 1600 m a.s.l.) 5 May – 10 June 2014, directly adjacent to tea plantations and deciduous forest, 90 km inland from the coast. The site is located in the area where the southwest monsoon arrives and is freely advectable from 200-280°N, while the mountain ridge is towards 180-360°N. Air was collected using a high volume sampler (Digitel) equipped with a quartz fibre filter and 2 polyurethane foam plugs in series. Soil samples (horizon A, nitisol) were taken in the tea plantation, in shrubs and in forest.

Samples were extracted with dichloromethane and analysed using a GC-MS/MS (SGE HT-8 column) for α-HCH, β-HCH, γ-HCH, d-HCH, o,p'- and p,p′-DDE, -DDD and –DDT, penta- and hexachlorobenzene (PeCB, HCB), PCB28, -52, -101, -118, -153, -138 and -180, α- and β-endosulfan, endosulfan sulphate. Recovery of native analytes was 75-98%. The mean of 3 field blank values was subtracted from the air sample values.

The direction of diffusive air-soil mass exchange was indicated by the ratio of the fugacities in both compartments, assuming that absorption in soil organic matter is the process determining retention[6].

The response of the air-soil cycling to onset of monsoon was studied by a 1 month regional scale 3D simulation of meteorology, atmospheric and soil chemistry (WRF/Chem 27 km×27 km, nudged with 6-hourly 1°×1° NCEP re-analyses, change of boundary conditions with onset) and by a long-term (1965-2014) 1D model simulation. The 1D non-steady state model of intercompartmental mass exchange[7] consists of a chain of 7 double-boxes (planetary boundary layer, top soil) representing latitudinal zones (each 3.75°N wide).

Results and discussion

In soil, the concentration of DDT compounds exceeds all other pollutants by far. Still, this DDX contamination level is among the lowest ever reported from agricultural soils in India[8]. The concentration of HCH is very low, again lower than ever reported from soils in India[8], and very uniform across soil samples, obviously determined by atmospheric deposition.

With the onset of SW monsoon, near-ground air concentrations in Munnar dropped from 12.6 to 3.1 for Σ4HCH, from 7.4 to 1.9 for Σ6DDX, and from 21.3 to 9.9 pg m^{-3} for Σ7PCB.

We compared air-soil exchange trends between two periods, before and immediately after onset of the monsoon, i.e. 6-10 June. For the period representing the pre-monsoon we selected the last 96 h before the pollution decrease, i.e. 25-29 May.

It is found that the direction of air-soil exchange changed with the onset of monsoon, with a general trend towards high soil-to-air fugacity ratios, f_s / f_a, hence, towards pollutant release from soils (Fig.

1): α- and γ-HCH were in phase equilibrium in the tea plantation before onset, but net-volatilisational during monsoon (γ-HCH also in shrubs), while β-HCH changed from net-depositional to close to phase equilibrium. In the forest, PCB28 and -52 turned net-volatilisational (close to phase equilibrium before monsoon). The drop in air concentration, which comes with the onset of monsoon, is found to trigger reversal of diffusive air-soil exchange of POPs.

The 3D simulation suggests that in southern India, the change of pollutant level reflects the drop in the advected air from SW, while with propagation northward this signal weakens (Fig. 2). Obviously, the increasingly polluted air weakens the re-volatilisation flux.

Long-term simulations of air-soil exchange of semivolatile persistent substances in India suggest fluctuation, i.e. seasonally re-volatilising and seasonally net-depositing (e.g., PCB28, PCB153), during past decades or on-going. With onset of SW monsoon, re-volatilisation is increasing (PCB153, DDE). For α-HCH, p,p'-DDT and α-endosulfan, net-deposition is predicted almost throughout the 50 years.

The drop of air pollution with the onset of the southwest monsoon will be most pronounced in those areas which receive marine background air, i.e. the southwest of the subcontinent. This research suggests that during the monsoon season and along transport over the subcontinent, air masses pick up pollution of OCPs re-volatilised from ground sources. A similar behaviour is likely for fluorinated and brominated chemicals. Such secondary emissions may well contribute significantly to the long-range transported atmospheric burden received in remote areas of central Asia.[9]

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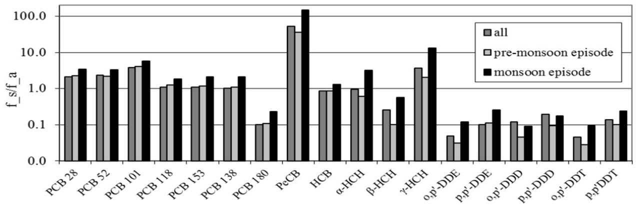

Fig. 1: Change of fugacity ratios, f_s/f_a, with the onset of monsoon above forest soil.

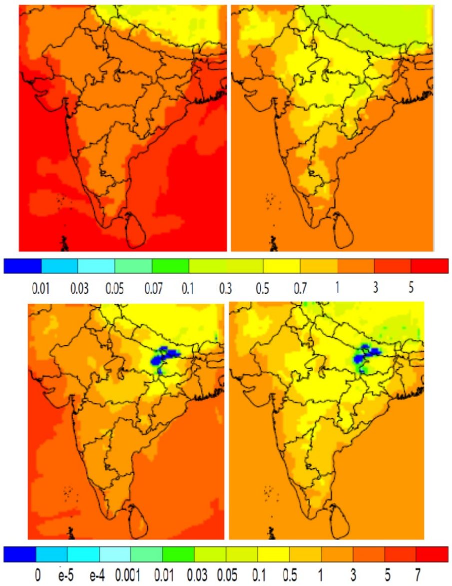

Fig. 2: Response of the air-soil chemical sub-system: Distribution of *γ*-HCH (left) and *p,p'*-DDE (right, pg m^{-3}) concentration in air (ground level, before onset of SW monsoon 2014, upper) and difference of concentrations before minus after onset (lower)